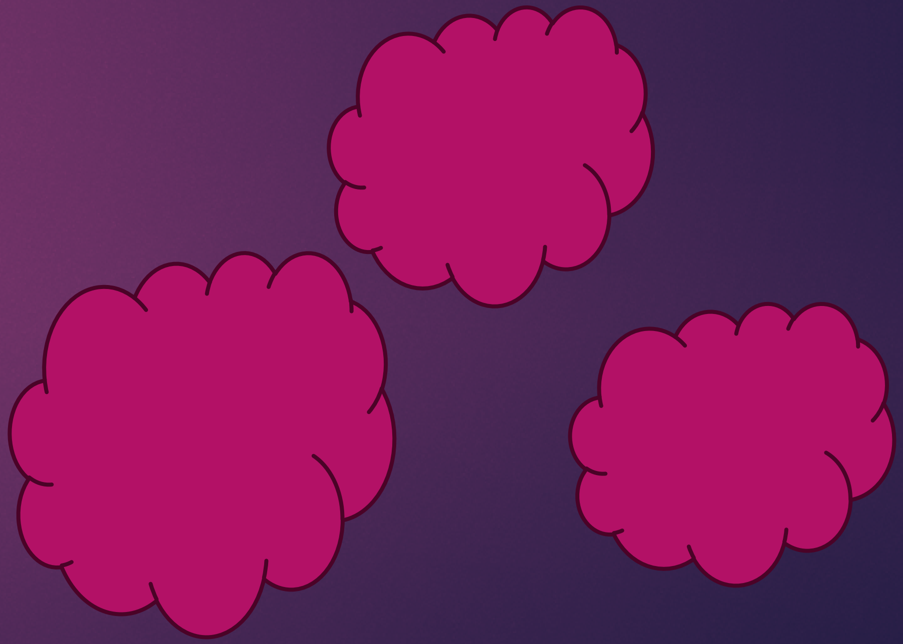
Applications of Functionalized Natural and Synthetic Macromolecules



Biodegradable Polymers Classifications and Challenges

Depending on the source of origin, biodegradable polymers can be classified as either derived naturally through fermentation or by extracted biomass through polymerization.

Various categories of biodegradable polymers derived from agricultural sources such as polysaccharides or protein which are usually extracted from micro-organisms.

The first category of biopolymers are those which are derived directly from bio-sources and consist of polysaccharides, lipids and proteins chitosan, gum, starch.

These are generally extracted from renewable lingo cellulose biomass, sea creatures and agricultural resources.

It is noteworthy to mention that naturally polymers such as cellulose, chitosan and silk have superior mechanical properties but show poor film forming ability and due to their hydrophilic nature they also show lower stability under ambient conditions.

Chitosan Derivatives and Their Application

Chitosan is a renewable natural alkaline polysaccharide that has no toxicity and no side effects, and it features good moisturizing and adsorption properties.

Both, chitin and chitosan are employed in countless applications as adsorbents for the removal of dyes and metal ions in waste water treatment, fat binder in food industry thin membranes in filtration processes edible layer in packaging coating material for fertilizer and seeds in agriculture Lotions and body creams in cosmetics, vehicle for drug delivery.

Chitosan is widely used in packaging applications due to its biodegradability, non-toxicity.

While the physicochemical properties of polymers are improved by the addition of chitosan, the hydrophilic nature of chitosan is a real drawback, which inhibits its contribution in packaging.

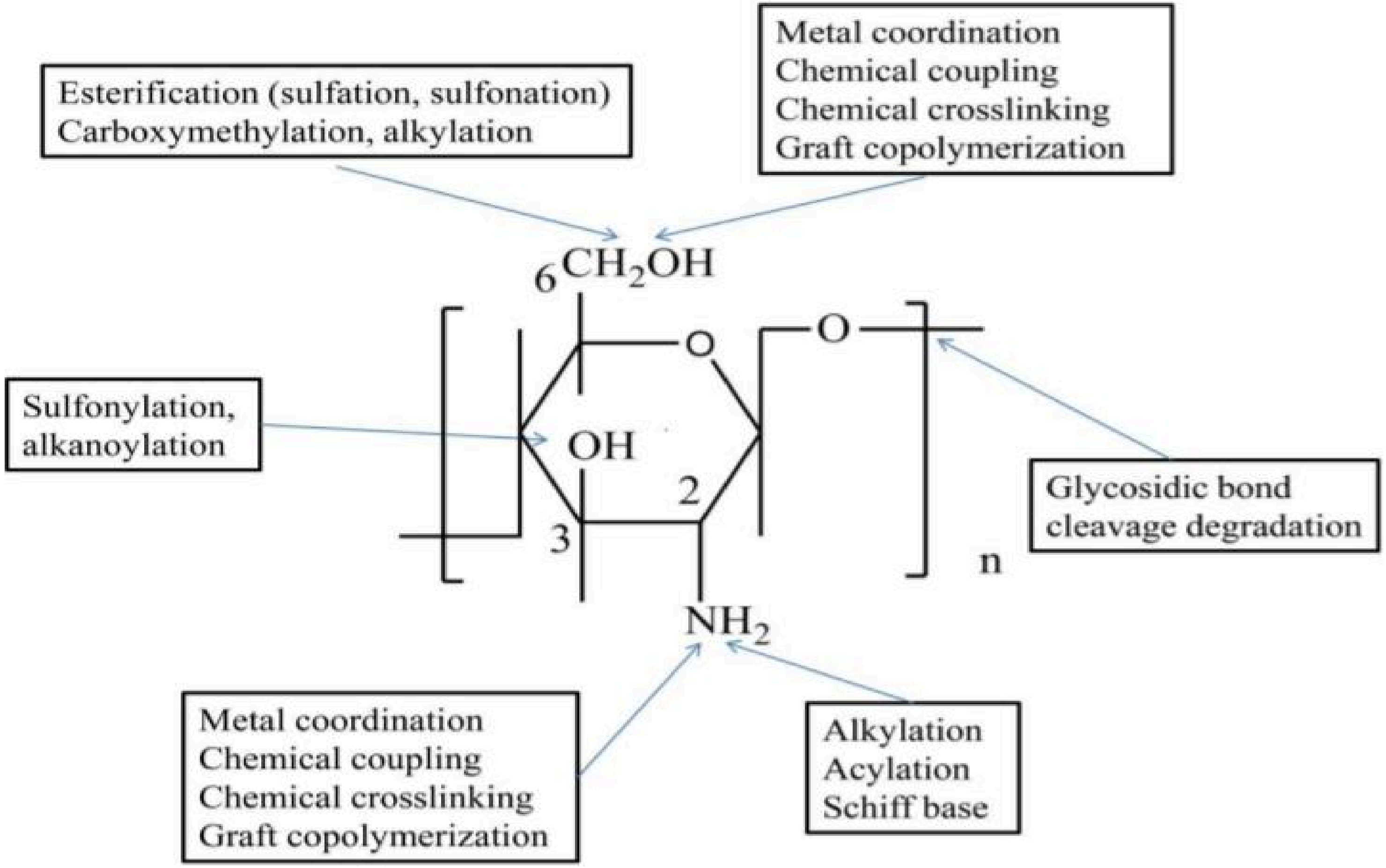
chitosan is insoluble in water and most organic solvents, which limits its applications in various fields.

Chitosan derivatives can be obtained by the chemical modification of chitosan reactive functional groups.

Modification of Chitosan

Functional groups on the chitosan molecules include C3–OH, C6–OH, C2–NH2, and acetyl amino and glycoside bonds.

The chemical modification of chitosan can improve its physical and chemical properties, as well as expand its applications.


Esterification (sulfation, sulfonation)
Carboxymethylation, alkylation

Metal coordination
Chemical coupling
Chemical crosslinking
Graft copolymerization

Sulfonylation,
alkanoylation

Glycosidic bond
cleavage degradation

Metal coordination
Chemical coupling
Chemical crosslinking
Graft copolymerization

Alkylation
Acylation
Schiff base

Acylated Modified Chitosan

Acylation modification is the most common modification of chitosan.

introducing aliphatic or aromatic acyl groups to the Molecular chain N-acylated chitosan derivatives show enhanced biocompatibility, anticoagulability, and blood compatibility.

Moreover, N-acylated chitosan derivatives don’t cause an inflammatory reaction in the human body, so N-acylated chitosan can be used in Pharmaceutical applications

The solubility of N-acylated chitosan depends on the degree of substitution (DS) and the length of the side chain.

nacylated chitosan, with high solubility, can be used as a carrier for Hydrophobic drugs

If only O-acylated chitosan is required, it is necessary to add a solvent to protect the ammonium group, such as trifluoroacetic Acid.

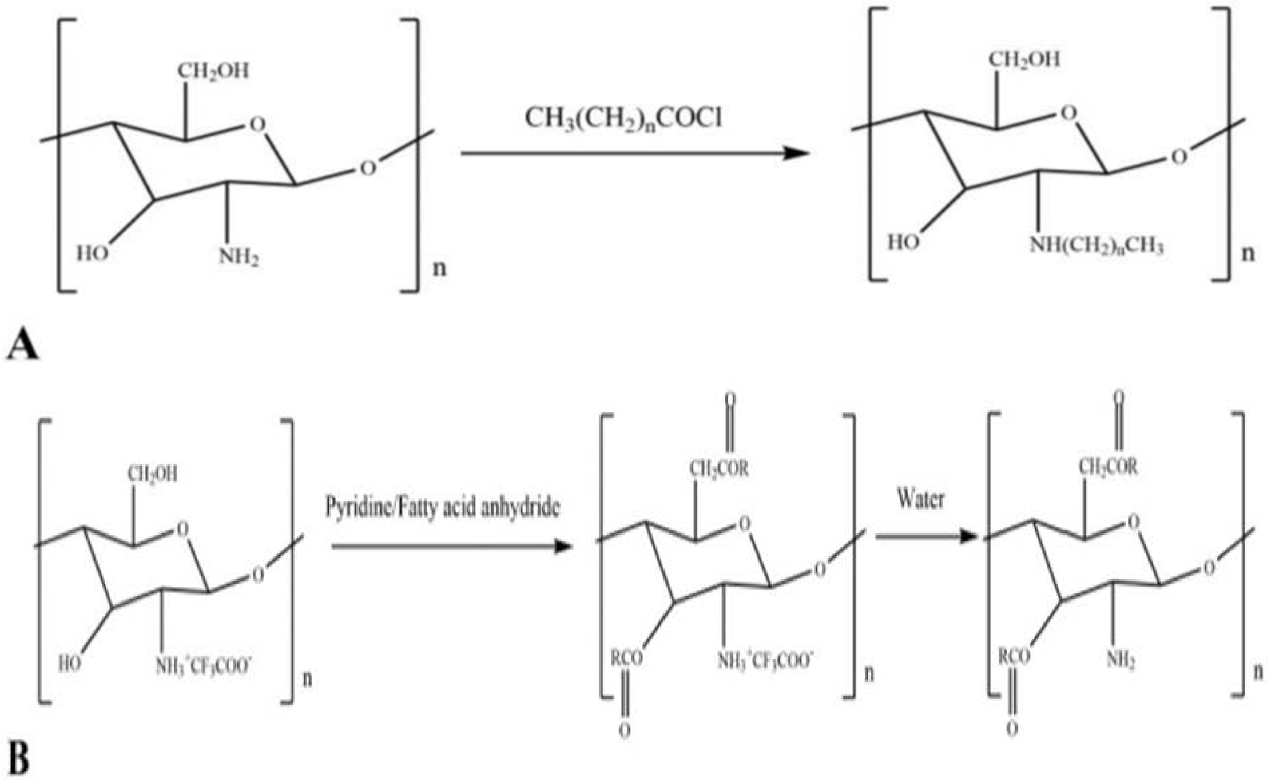
Acylated Modified Chitosan

O-acylated chitosan is lipid-soluble and can be dissolved in non-polar Solvents such as pyridine and chloroform.

Reaction equations for acylated chitosan derivatives.

(A) N-acylated chitosan.

(B) O-Acylated chitosan.



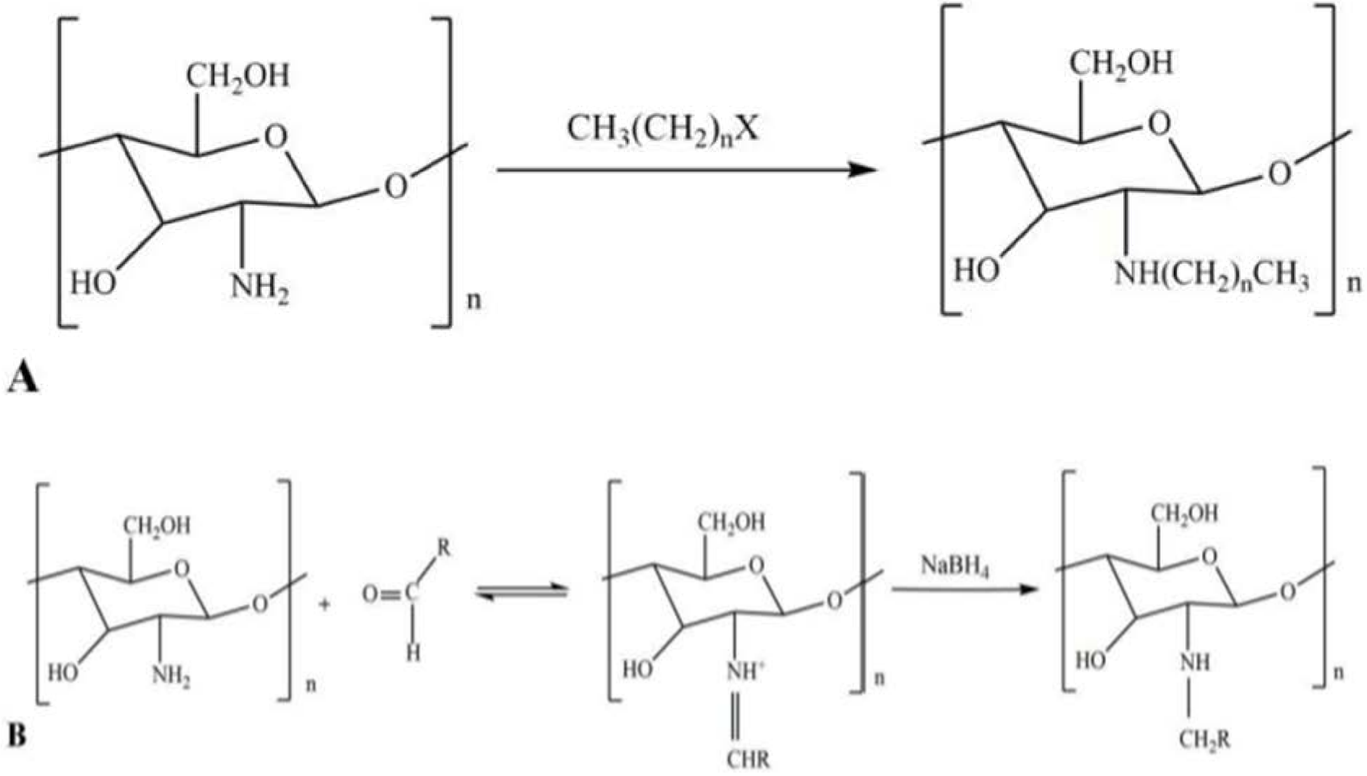
Alkylation Modified Chitosan

Alkylated chitosan can be used to prepare medical gauze due to its coagulation and antibacterial Properties.

Alkylation chitosan derivative reaction equations.

(A) Halogenated alkane to prepare N-Alkylated chitosan.

(B) advanced fatty aldehyde prepares N-alkylated chitosan.



Carboxylated Chitosan

Carboxylated chitosan has wider Applications than chitosan in the industry, agricultural, medical, health, and biochemical fields.

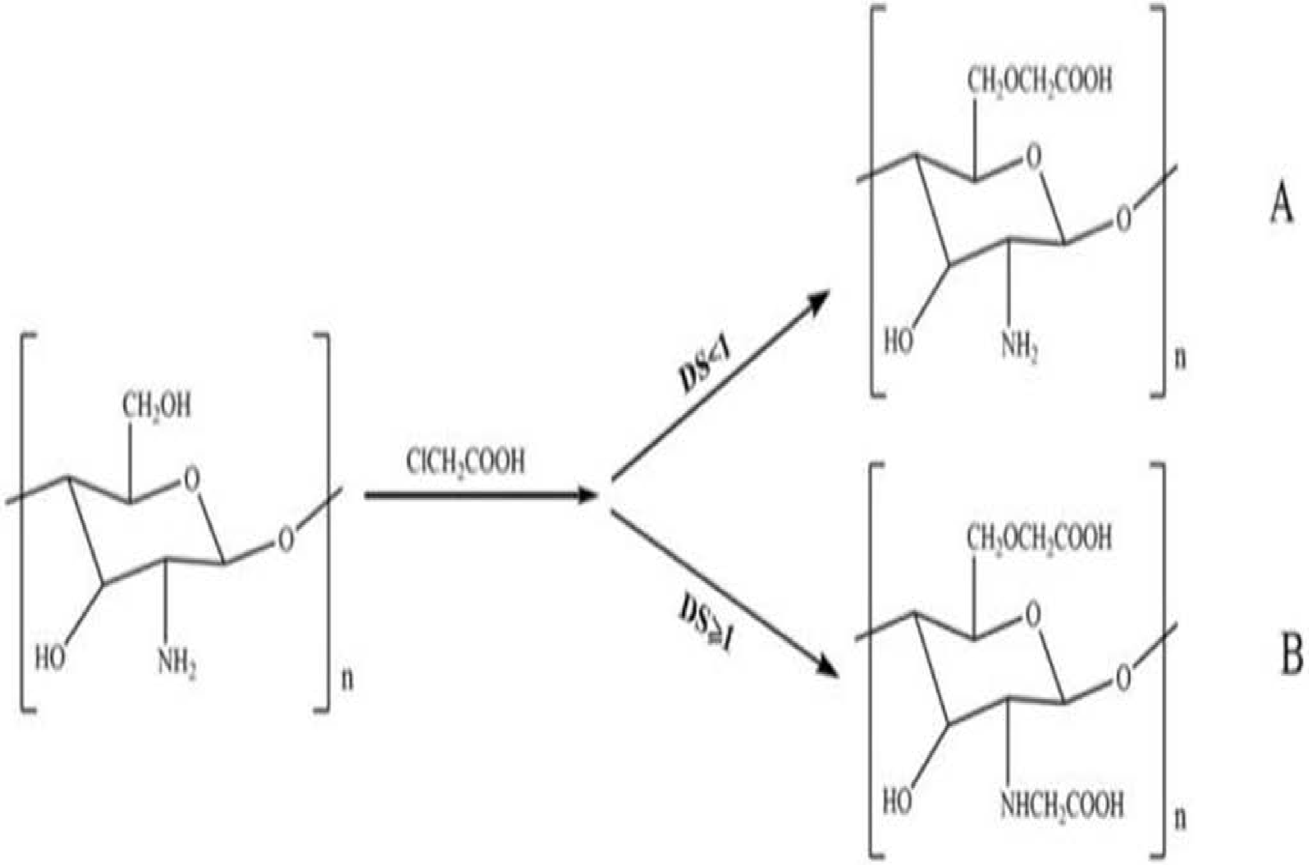
active in the biomedical and pharmaceutical fields due to its antibacterial properties, which promote wound healing.

Carboxylates chitosan derivative reaction equation.

(A) O-car boxy methyl chitosan

(degree Of substitution (DS) < 1)

(B) N, O-car boxy methyl chitosan (DS ≥ 1).



Quaternary Ammonium Chitosan

Quaternary ammonium chitosan salt also has better antibacterial,

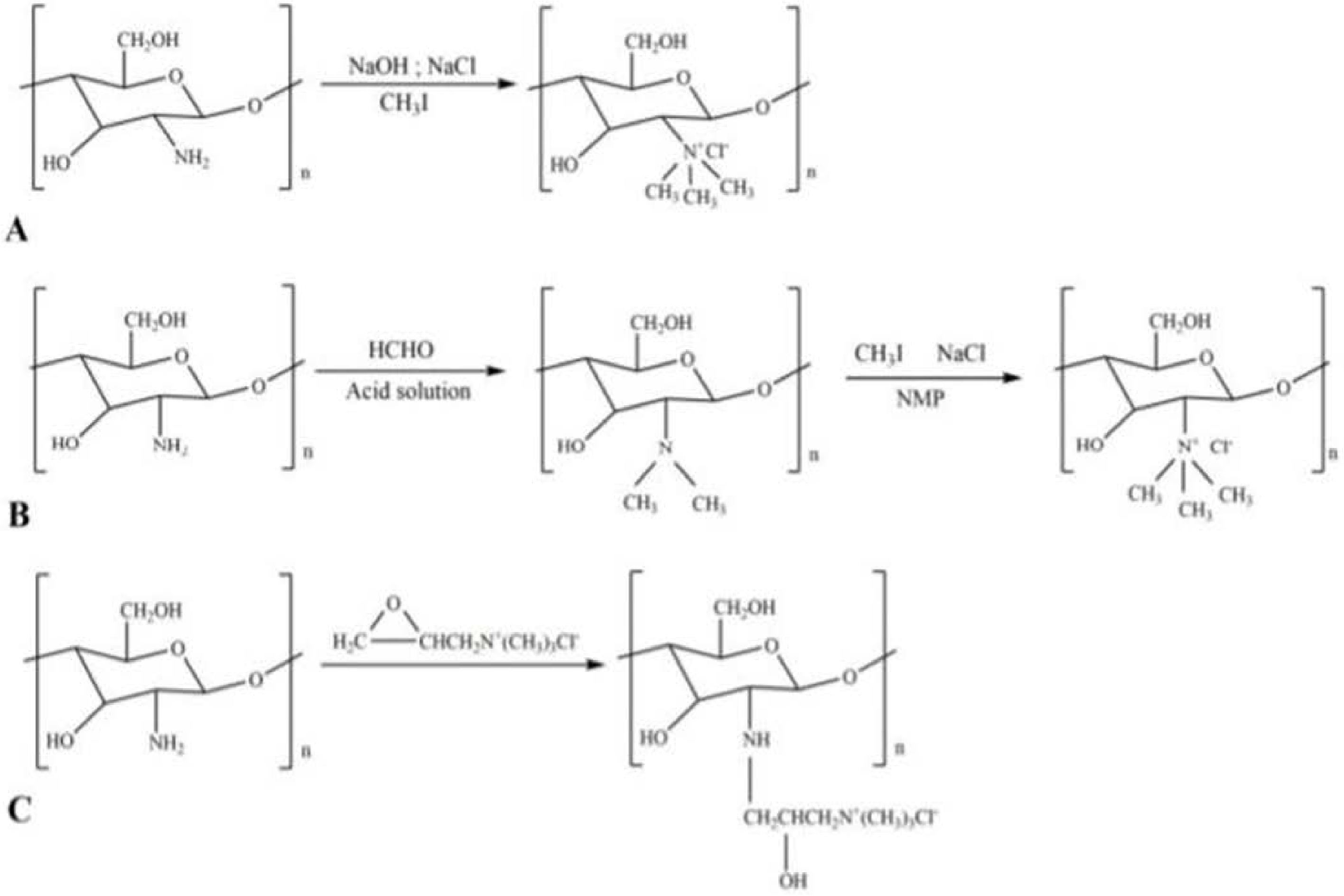
biodegradability, non-toxicity, and biological effects, and the ability to penetrate mucus layers

Reaction equations for quaternized chitosan derivatives.

(A), N,N-trimethyl chitosan (TMC) direct quaternary ammonium salt substitution method

(B) TMC N-alkylation

(C) chitosan 2,3-epoxypropyl trimethyl ammonium chloride (GTA) ring opening method



Chitosan-Polyphenol Conjugates for Human Health

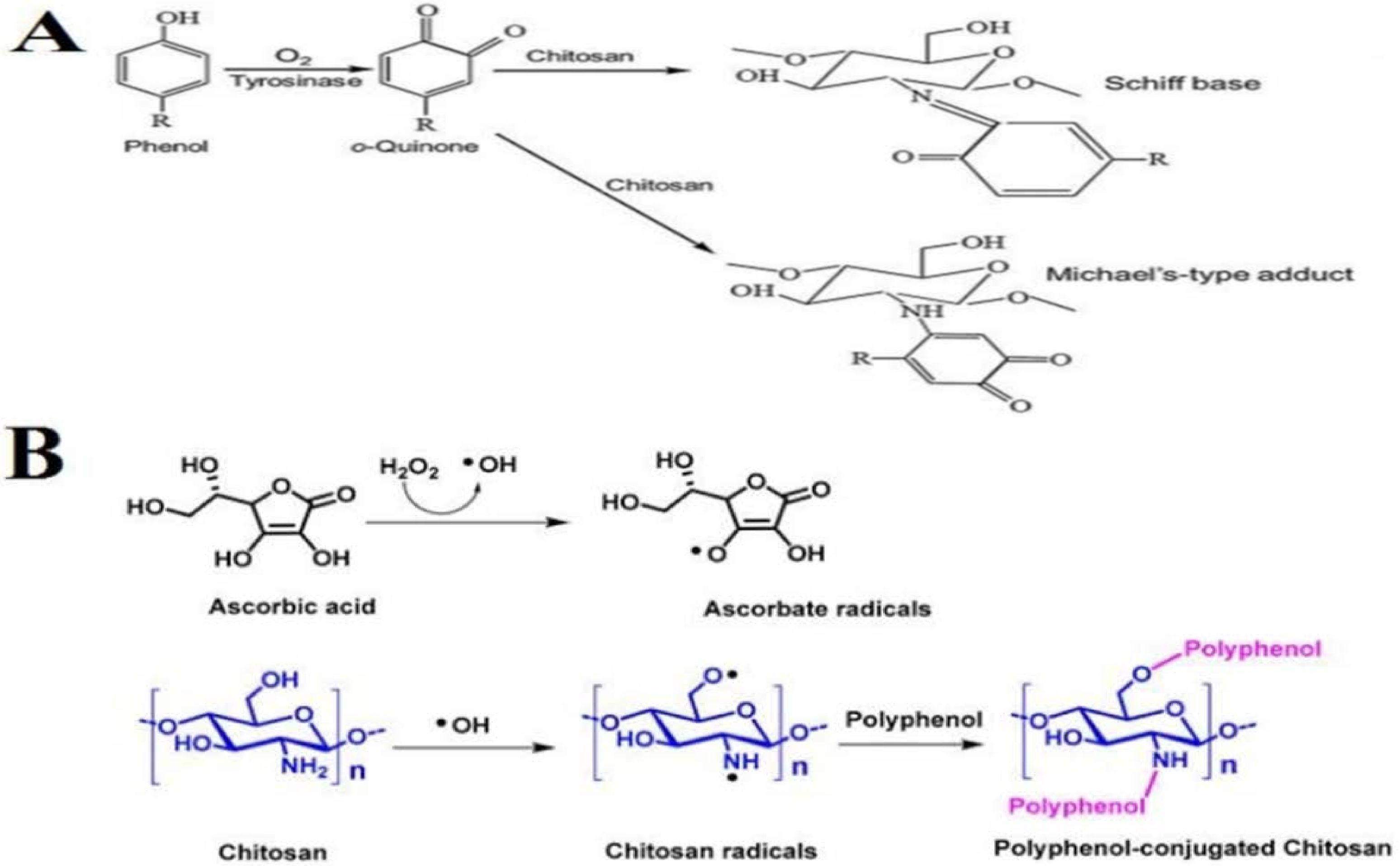
- **Polyphenol limitations:**
  1. Low bioavailability
  2. Short biological shelf life
  3. Rapid metabolism in body.
- **Chitosan limitations:**
  1. Poor water insolubility
  2. Faster enzymatic degradation in body
  3. Non-availability of H atom donor
- **Chitosan -polyphenol conjugates advantages**
  1. Higher solubility
  2. Extended shelf life
  3. Increased bioavailability
  4. Higher antioxidant effect
  5. Synergistic anti-bacterial activity

Chitosan-Polyphenol Conjugates for Human Health

Proposed mechanism for polyphenol-chitosan conjugate through

(A) enzyme-mediated Strategy

(B) free radical in Duced reaction



Synthesis and characterization of new functionalized chitosan and its antimicrobial and in-vitro release behavior from topical gel

Heterocyclic nitrogen-containing compounds:

(Including the five-membered Benzimidazole and thiadiazole moieties).

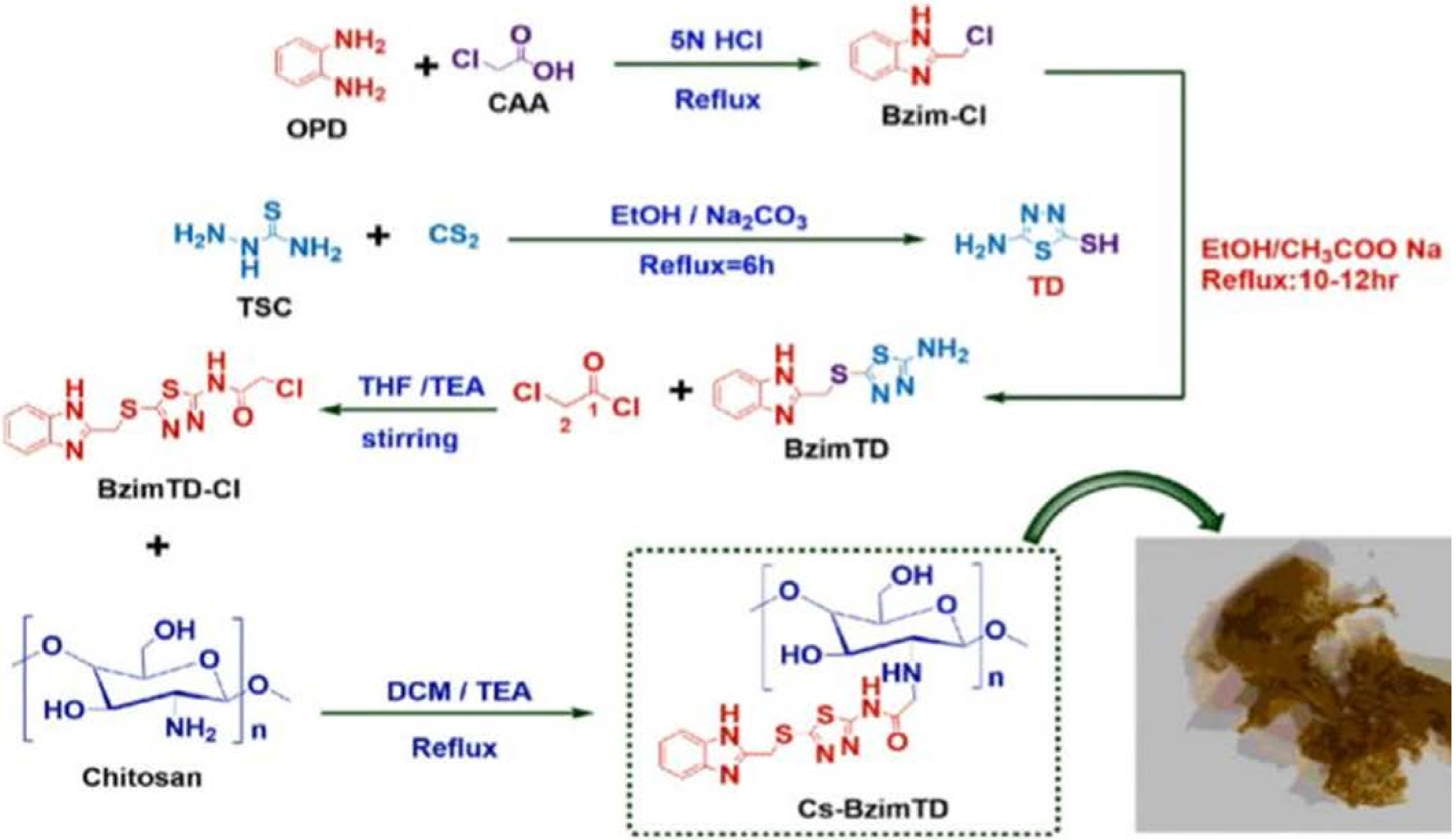
More than 75% of the drugs authorized by the Food and Drug administration and currently available in the pharmaceutical market belong to this group of therapeutic compounds.

benzimidazole is one of the most famous and biologically active Members of the heterocyclic group and is found in many synthetic and Natural therapeutic agents such as: anticancer, antimicrobials, antioxidants.

Recently, various benzimidazole based thiadiazole and triazole derivatives have been recorded as efficient anti-microbial agents

Synthesis and characterization of new functionalized chitosan and its antimicrobial and in-vitro release behavior from topical gel

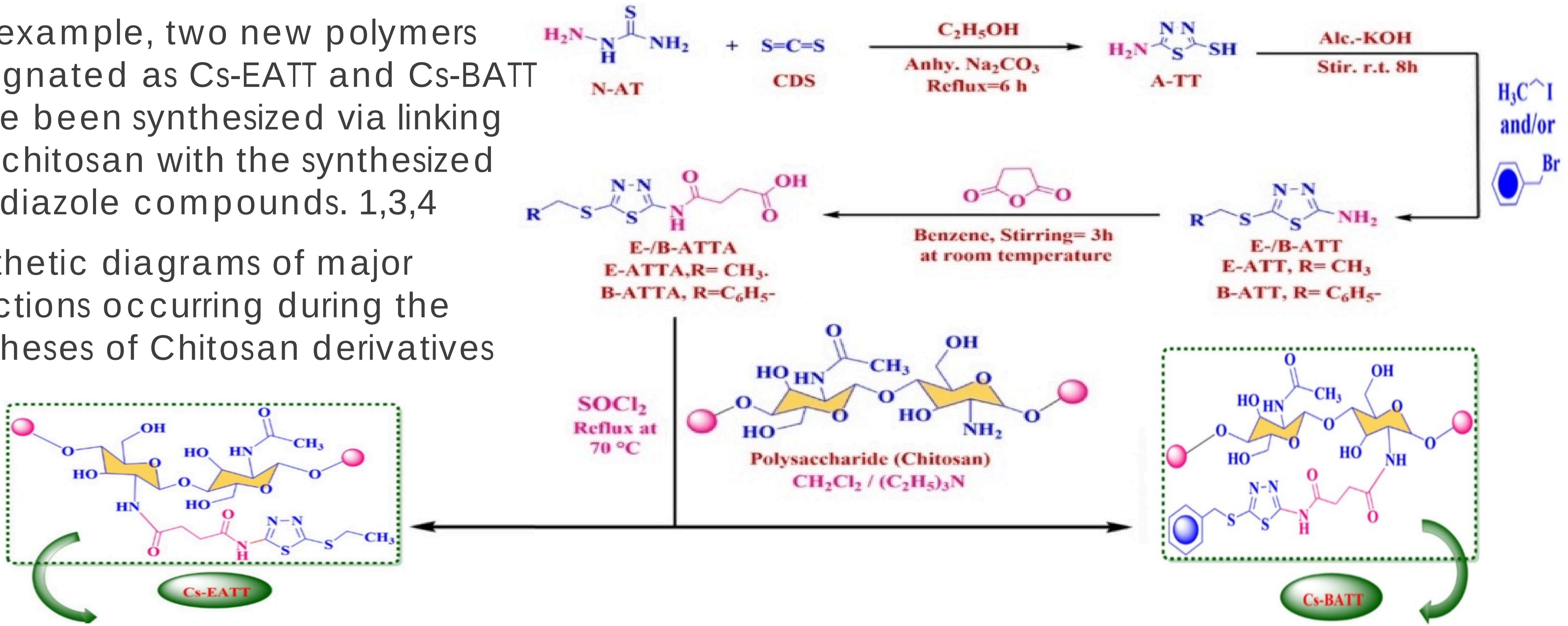
OPD	**Ortho Phenyl Diamine**
CAA	**Choloro Acetic Acid**
TSC	**Thiosemi carbazide**
TD	**Thisol diamine**



1,3,4-thiadiazole modified chitosan

For example, two new polymers designated as Cs-EATT and Cs-BATT have been synthesized via linking the chitosan with the synthesized thiadiazole compounds. 1,3,4

Synthetic diagrams of major reactions occurring during the syntheses of Chitosan derivatives



Chemical Natural Gum Based Composites Modification, Property Evaluation and Applications

The natural gums are non-toxic, biodegradable and low cost polysaccharide they are applicable in various areas such as pharmaceuticals, adhesives, films, paints.

Gum Arabic (GA) is one of the natural complex polysaccharides, derived from an exudate of Acacia trees the other existing gums are guar gum.

Guar gum (GG) is a non-ionic natural polysaccharide sourced from the seeds of cyamopsis, guar gum is used in many applications in industries such as, textile, petroleum, paper, food, explosives and pharmaceuticals it is biocompatible, biodegradable, non-toxic, low-cost and amenable to chemical modification.

delivery .Carboxy methyl guar gum was formulated as micro particles tailored for drug applications

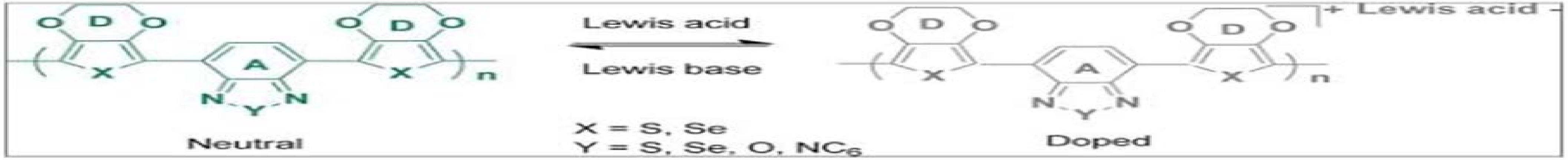
Conducting Polymers

the delocalized electrons may move around the whole system.

However, conjugation is not enough to make the polymer material conductive.

In addition, the polymer material needs to be doped for electron flow to occur.

Doping is either the addition of electrons (reduction reaction) or the removal of electrons (oxidation reaction) from the polymer, for example :



As the electrons are moving along the molecule, electric current occurs.

For better conductivity the molecules must be well ordered and closely packed to limit the distance "jumped" by the electrons.

Electrical Conductivity of Oxadiazole and Triazole Polymer Content

The field of electrically conducting polymers has been developed very rapidly since the discovery of intrinsically conducting polymers.

It was noticed that the electrical conductivity of organic Conjugated polymers was increased when they are doped with oxidizing or reducing agents.

By controlling the oxidation or reduction processes, the electrical conductivity and optical properties of the polymer can be controlled undoped conjugated polymers are established as intrinsic semiconductors**.**

In this work different polymers with oxadiazole and triazole heterocyclic ring have been prepared to prove the effects of chemical structure on the electrical conductivity

On the other hand, the ability to Doping was studied by different dopant The electrical conductivity of the conjugation polymers can be affected by different factors The Presence of long aliphatic segment within the back bone of the polymer chain can increased the electrical conductivity of the polymer by increasing the flexibility On the other hand the presence of aliphatic segment interrupts the conjugation and decrease the electrical conductivity The presence of the hetero atoms in the main chain of the polymer will enhance the electrical conductivity by the Participation of the lone pair of electron of the hetero atoms in the conjugation system Also hetero Atoms can be considered as a site to host the dopant molecule and create the charge carriers.

Conducting Polymers

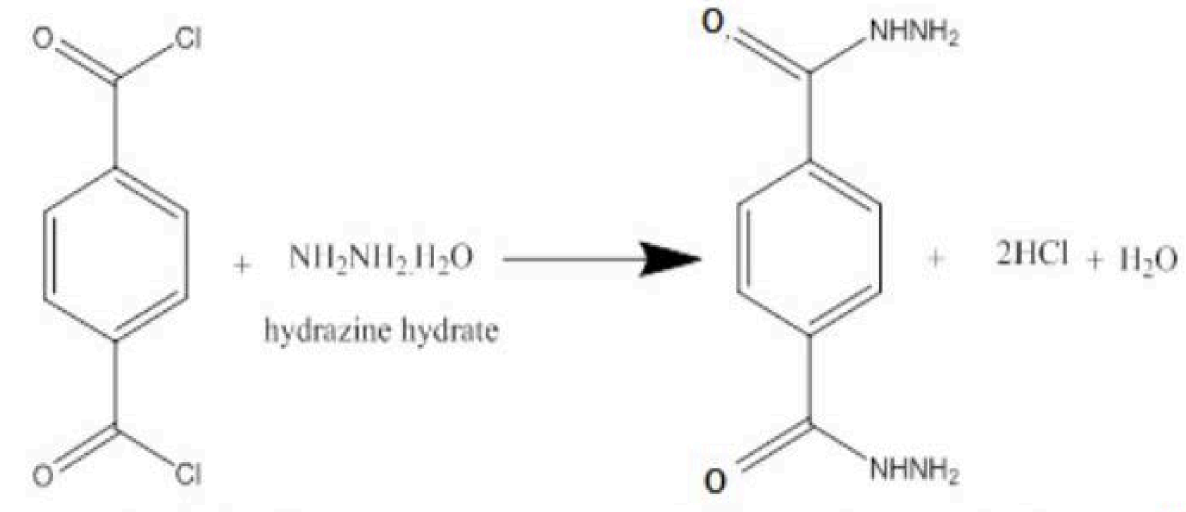
Synthesis of 1, 4-bis (1-hydrazineylvinyl)benzene

In a round bottom flask contain 20ml of hydrazine hydrate and 2ml dry dioxane, adding drop wise a solution of 6.5g (0.03mole) of terephthaloyl chloride dissolv in 6ml dry dioxane at room temperature.

The mixture was refluxed for extra 2 hrs.

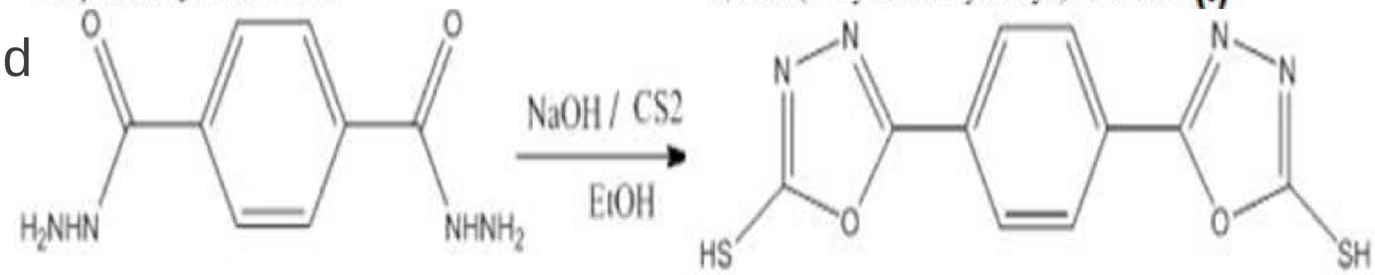
The yellow precipitate was filtered, washed with ethanol and dried under vacuum.

Synthesis of 1,4-bis (1-hydrazineylvinyl)benzene (I)



erephthaloyl dichloride

1,4-bis(1-hydrazineylvinyl)benzene **(I)**



terephthalohydrazide

5,5'-(1,4-phenylene)bis(1,3,4-oxadiazole-2-thiol) **(M1)**

Conducting Polymers

Polymer preparations:

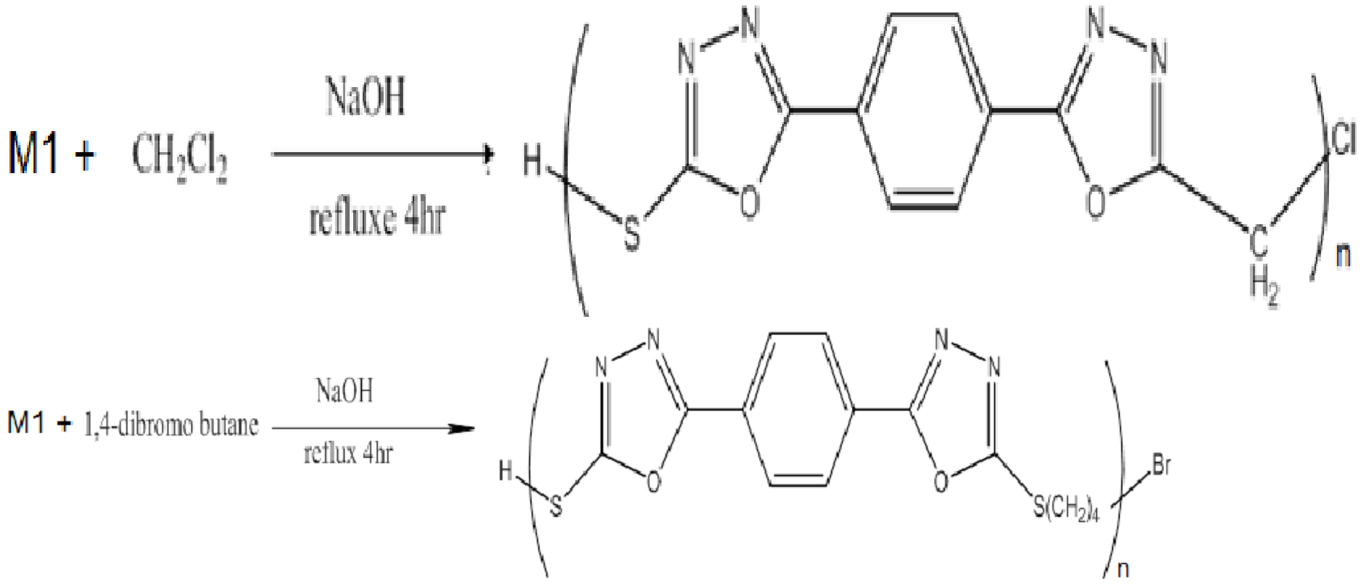
Polymer I: 1.43g (0.005mole)of M1 was dissolved in 0.1M NaOH solution.0.42ml of dichloromethane was added drop wise and the reaction mixture was refluxed for of 4hrs .

The produced yellow polymer was filtered and dried under vacuum.

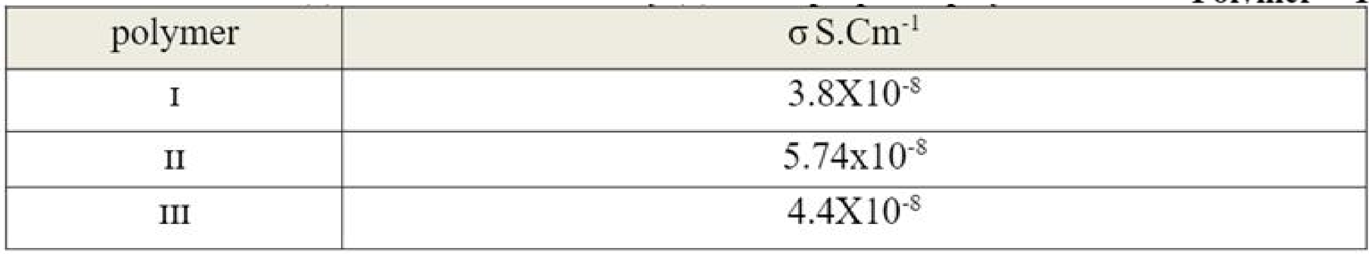
Polymer II: The same procedure for preparation polymer I was followed by polymerization of M1with 1.07ml of dibromobutane.

The results indicate that the major factor effect on conductivity is the chemical structure of the polymer.

It was noticed that the electrical conductivity of polymer III is higher than that of polymer I



Polymer III



polymer	σ S.Cm^{-1}
I	3.8X10^{-8}
II	5.74x10^{-8}
III	4.4X10^{-8}

Applications of conductive polymers

- polyaniline is used as a conductor and for electromagnetic shielding of electronic circuits.
- Polyaniline is also manufactured as a corrosion inhibitor.
- Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrene sulfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serves as a hole injecting electrode material in polymer light-emitting devices.Poly (phenylene vinylidene) derivatives have been major candidates for the active layer in pilot production of electroluminescent displays (mobile telephone displays).
- Poly (dialkylfluorene) derivatives are used as the emissive layer in full-color video matrix displays.
- Poly (thiophene) derivatives are promising for field-effect transistors: they may possibly find a use in supermarket checkouts.
- Poly (pyrrole) has been tested as microwave-absorbing "stealth" (radar-invisible) screen coatings and also as the active thin layer of various sensing devices.Other possible applications of conductive polymers include super capacitors and electrolytic-type capacitors